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(54) Title: PROCESS FOR REMOVING METALS FROM WASTE OIL

(57) Abstract

The invention relates to a process for removing metals from waste oil, whereby the waste oil is at first pretreated for removing the water and solids included therein, after which this is dispersed with a sufficient amount of an EDTA solution at an elevated temperature under basic conditions, whereby metal complexes are formed, and finally the phases are separated from each other.

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Process for removing metals from waste oil

The present invention relates to a process for removing metals from waste oil. By means of the process of the invention the waste oil can be treated to a reusable product by removing metals included in the oil, especially lead, from the oil.

From the literature of the field are known various methods of treating waste oil for removing metals from the oil. According to U.S. Patent 3,763,036, methyl ethyl ketone is added to waste oil for removing lead. A coagulated insoluble layer provided in this manner and the purified oil can be separated from each other.

According to U.S. Patent 4,411,774, waste lubricating oil is treated for removing contaminants included therein by adding to the oil chemicals, such as $(NH_4)_2SO_4$, NH_4HSO_4, $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, $CaHPO_4$, H_3PO_4, $CaSO_4$, $Al_2(SO_4)_3$ and $MgSO_4$, at a high temperature of at least 340 °C. On account of distillations and high temperatures, the process is, however, unpractical and inconvenient.

Metals have been removed from waste oil also by adding an aqueous solution containing a surfactant and anions, which form insoluble salts with metals. The aqueous phase and the oil phase are then separated from each other and the oil is filtered (U.S. Patent 4,250,021).

Lead can also be removed from waste oil by agglomerating suspended oil in such a way that the oil is heated to a temperature of 260 to 370 °C. At least 90 % of the lead can be removed by this method disclosed in U.S. Patent 3,923,643.

The object of the present invention is to provide from waste oil such a product that can be re-

utilized, for instance burned. This is achieved according to the invention in such a way that metals, especially lead, being detrimental to the reutilization of waste oil, are removed by adding a complex forming substance to the oil. The process according to the invention is characterized in that the waste oil is at first pretreated for removing the water and solids included therein, after which this is dispersed with a sufficient amount of an EDTA solution at an elevated temperature under basic conditions, whereby metal complexes are formed, and finally the phases are separated from each other.

The process according to the invention is suitable for used lubricating oils of good quality, which can be mineral oil based or synthetic. Such waste oils can contain about 500 to 1000 ppm of lead, about 500 to 5000 ppm of zinc, about 1000 to 5000 ppm of calcium and about 200 to 2000 ppm of magnesium. According to the invention, treated waste oil can substitute for heavy oil, for instance.

The invention uses EDTA (ethylene diamine tetracetic acid) as a complex forming substance. Also other complexing agents, such as DCTA (1,2-diamino cyclohexane tetracetic acid), can be used.

The process according to the invention is based on a capability of an NH_4EDTA compound of complexing metals in a basic solution. Especially metals like Pb, Zn, Ca and Mg are concerned. The stability of the EDTA metal complex depends above all on pH value. The optimum pH of lead is 9,5 while that of zinc is 5,5. Therefore it shall be attended to that the pH of the EDTA solution is within the range 5 to 10.

In the process of the invention, the EDTA remains in an aqueous phase and is not transferred to the oil. It is then necessary to attend to that there

is a sufficient contact between the oil and the reagent to make it possible for free EDTA molecules in an interface to bind a great amount of metals being in an oil phase. In practice this is realized in such a way that the mixing time is kept sufficiently long and the mixing efficient enough. However, the mixing must not be so strong as to change the oil-EDTA-mixture into an emulsion, whereby it is difficult to separate the phases from each other. To achieve a maximum demetallization, the volume between the NH_4EDTA solution and the oil shall be 1:1 to 1:4, preferably 1:3. If this proportion is larger, i.e. if there is too little water, the efficiency to separate metals becomes weaker and the risk of emulsification increases. On the other hand, if the proportion is smaller, disadvantageous amounts of waste water are produced.

An advantage of the process of the invention consists of its efficiency, favourableness and simplicity. Further advantages are that the EDTA can be recovered from the metal-EDTA-complex by precipitating the EDTA with hydrochloric acid. The yield of EDTA recovered is about 75 to 90 %.

Before treating the oil with EDTA, the oil is subjected to a prepurification performable in two different manners:

Prepurification procedure A:

a) waste oil batches to be purified are collected in a container for providing an even consistency,

b) an emulsion dispersing chemical is added,

c) the oil mixture is heated to a temperature of 60 to 70 °C,

d) the mixture is separated for removing solids and water from it (water content after this 1 % at the maximum).

Prepurification procedure B:

a) waste oil batches are collected in a container for providing an even consistency,

b) the oil mixture is heated to 65 °C,

c) the mixture is allowed to clarify for a time of 1 week to 2 months,

d) the water separated is removed,

e) an emulsion dispersing chemical is added,

f) the mixture is allowed to clarify,

g) a layer of water and soot settled on the bottom is removed (water content of oil after this 1 to 1,5 %),

h) the mixture is possibly centrifuged for removing the solids.

Accordingly, the purpose of the pretreatment is to homogenize the oil and to remove the water and the solids from it. Experiments made on a pilot scale have proved that a separation of the phases of a dispersed mixture succeeds best by clarifying.

Preparation of an EDTA reagent:

650 l of 25 % NH_3 are added to 1500 litres of water. To this water solution are mixed 1000 kg of solid EDTA, after which the pH of the mixture is 6 to 6,5 (volume 3,5 m^3). 350 litres of this solution are used per 5 m^3 of the oil to be purified, i.e. the used amount of reagent calculated to EDTA is 20 kg of EDTA per m^3 oil.

The next example describes the present invention.

Example 1

5 m^3 of prepurified oil are pumped into a 7 m^3 container. For neutralizing the acids included in the oil and for raising the pH, 50 l of the 25 % NH_3 solution are added to the oil. The mixture is stirred for 2 minutes. 350 litres of the EDTA reagent prepared above are diluted with water to 1,5 m^3, which are then

added to the oil mixture. The mixture thus obtained is stirred for 4 minutes by a propeller mixer at a speed of 750 rpm at a temperature of 40 to 50 °C. The pH is then about 9. After this the mixture is pumped into a clarification container. During pumping the temperature rises to 80 °C. The mixture is allowed to clarify for 1 to 2 days. The water content of the oil is at this stage 1 to 2 %. The metal contents of the unpurified oil, which has been prepurified by removing water and solids from it, and the contents of metal residues of the oil obtained after the purification are presented in Table 1 for ten oil batches of 5 m^3. The mean value $\bar{X}$ and the standard deviation SD of these 10 tests are also given.

Table 1

		Unpurified oil			
Test	H_2O %	Pb ppm	Zn ppm	Ca ppm	Mg ppm
1)	2,4	304	766	1720	252
2)	1,3	390	710	1780	214
3)	5,1	374	834	1680	288
4)	5,2	400	802	1630	194
5)	0,8	390	782	1700	318
6)	3,4	370	716	1460	180
7)	1,7	330	620	1320	158
8)	1,4	350	646	1480	164
9)	3,1	360	724	1550	186
10)	2,8	360	734	1540	152
	$\bar{X}$	363	733	1586	211
	SD	29	66	142	57

Purified oil

1)	1,6	9	3,4	19	5
2)	1,0	7	2,4	23	5
3)	1,1	10	4,6	15	6
4)	1,0	25	16	44	15
5)	0,9	29	5,0	33	10
6)	1,2	19	4,4	23	8
7)	1,1	20	4,6	24	8
8)	1,1	18	5,0	19	7
9)	1,1	19	4,8	19	7
10)	2,6	9	7	9	2
	$\bar{X}$	16,5	5,7	22,8	7,3
	SD	7,5	3,8	9,7	3,5

Claims:

1. A process for removing metals from waste oil, characterized in that the waste oil is at first pretreated for removing the water and solids included therein, after which this is dispersed with a sufficient amount of an EDTA solution at an elevated temperature under basic conditions, whereby metal complexes are formed, and finally the phases are separated from each other.

2. A process according to claim 1, characterized in that the dispersion is performed at a temperature of 40 to 50 °C.

3. A process according to claim 1 or 2, characterized in that the amount of the added aqueous solution of NH_4EDTA is 15 to 20 kg of EDTA per m^3 oil, preferably 20 kg of EDTA per m^3 oil.

4. A process according to any of the claims 1 to 3, characterized in that the pH of the NH_4EDTA solution is 5 to 10, preferably about 9.

5. A process according to any of the claims 1 to 4, characterized in that NH_4EDTA solution is added to waste oil in the proportion 1:3 to 1:4, preferably in the proportion 1:3.

INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER

IPC5: C10M 175/02
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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EDOC, WPI, CA SEARCH

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4778590 (REYNOLDS, J.G. ET AL.), 18 October 1988 (18.10.88), claims 1,5, abstract --	1
X	Chemical Abstracts, Volume 106, No 8, 23 February 1987 (23.02.87), (Columbus, Ohio, USA), Essington, M.E. et al., "Extraction of inorganic chemical constituents from retorted oil shale by complexometric agents", page 328, THE ABSTRACT No 55273d, Energy Res. Abstr. 1986, 11 (20), (Eng.) --	1

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	US, A, 5042617 (BROWNAWELL, D.W. ET AL.), 27 August 1991 (27.08.91), claims 1-2	1
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INTERNATIONAL SEARCH REPORT

Information on patent family members

26/08/93

International application No.
PCT/FI 93/00[illegible]

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		CA-A- 2024006	08/03/91
		EP-A- 0416905	13/03/91
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US-A- 4359093	16/11/82	NONE	
SU-A- 1384607	30/03/88	NONE	